Investigation of the Raman spectra of two dimensional, hexagonal lattices

Thesis points of the PhD thesis

Gergő Kukucska

ELTE TTK, Doctoral School of Physics

Department of Biological Physics

Materials Science and Solid State Physics program

Budapest, 5th November, 2018

Supervisor: János Koltai
Assistant Professor
ELTE TTK Institute of Physics
Department of Biological Physics
Leader of Program: István Groma
Professor
ELTE TTK Institute of Physics
Department of Materials Physics
Leader of School: Tamás Tél
Professor
ELTE TTK Institute of Physics
Department of Theoretical Physics

1 Introduction

In the last decade, investigation of two-dimensional materials became one of the most widely studied area of solid state physics. From the point of the industry, these materials are good candidates for producing advanced microprocessors. Currently these are made by the silicon based semiconductor industry, however, these devices use a lot of energy and their computational capacity is reaching its limits. Moreover, two-dimensional materials cover wide spectra of electric properties (e.g. insulators, conductors, half-metals, topological insulators, etc.), which can be perturbed easily due to their large relative surface.

A good candidate for the integration to the industry is the graphene, the hexagonal lattice of carbon atoms which was the firstly discovered two dimensional material [1]. Nevertheless this material is a conductor and the known manipulation techniques cannot be used due to the Klein paradox, hence currently it cannot be introduced to the industry.

An alternative of graphene, is its silicon analogue, that is, the silicene [2], which is unlike its carbon counterpart not completely planar, it has a buckling of approximately 0.4 Å. Due to this property, a bandgap can be introduced into the silicene sheet by applying a perpendicular electric field [3]. Its synthesis, however, is complicated due to the fact that there is no silicon analogue of graphite, thus the usually applied "scotch tape" method cannot be utilized. Production of silicene samples is usually done by vaporizing silicon atoms in vacuum to a hot (couple of hundred °C) silver surface. Similarly to graphene and silicene, other hexagonal lattices can be made from elements with three or four valence electrons such as germanium, tin or phosphorus, wich are called germanene [4], stanene [5] and blue phosphorus [6].

Two-dimensional materials are not exclusively built up from one element, lattices consisting two or three different elements can be made, such as the transitional metal dichalcogenides (e.g.MoS_2, $MoSe_2$, WS_2, etc.) [7]. These materials are usually large band gap semiconductors, which is a great advantage, however their production is expensive and they cannot be made in large quantities.

Sample fabrication of most two-dimensional material is not yet been solved, the techniques are still under development. In order to improve these techniques, one need to obtain as much information as possible from the samples already produced and the perturbations within it. A widely applied non-destructive technique is the Raman spectroscopy, with which one can acquire information from the sample by analysing its vibrational frequencies. During the thesis I investigated the Raman spectra of two-dimensional materials and the effect of perturbations to these spectra from multiple theoretical perspectives.

2 Thesis points

The main results of my thesis are summarized in the following four thesis points:

1. To determine the first order Raman spectra, I developed a previously not presented excitation energy dependent method, based on the Placzek approximation. To investigate its accuracy and to validate its results, I modelled the Raman spectra of the single layer MoS_2. I examined the effect of the numerical parameters to the Raman spectra and derived a few simple rule, which can be applied to acquire accurate results. Thereafter I studied the effect of two perturbations, the strain and doping, to the Raman spectra of monolayer MoS_2 and I found that the relative intensity ratio of the two peaks present in the spectra can be used to characterize strain [R1].

2. By applying the developed method I calculated the Raman spectra of numerous silicon-silver hybrid structures. As a first step I investigated the behaviour of the silver surface from multiple perspectives and I determined the required number of layers for the accurate description. After examining the structural and vibrational properties of the top silicon layer, I obtained the scanning tunnelling microscope images of the superstructures. I compared these to the ones already present in the literature and I concluded that the investigated structures are in great agreement with the ones found in experiments. Finally,

I determined the Raman spectra of the structures and I highlighted some specific features, with which the different reconstructions can be identified by their Raman spectra [R2].

3. I calculated the resonance Raman spectra of silicene and germanene within a tight-binding model. I determined the minimal model, in which the electronic properties of the two systems can be described accurately and I investigated the effect of spin-orbit coupling to the electronic structures. Based on the electron-phonon interaction I calculated the lifetime of the charge carriers and I showed similarities between the characteristic features of the electronic structure and the lifetime of charge carriers. In order to validate the model I compared the two phonon spectras with the ones in the literature. By analysing multiple theoretical results, I found correlation between the buckling value and the Raman intensity of the out of plane modes [R3].

4. I investigated the defect induced Raman spectra of silicene and germanene. In both systems I studied six theoretically simply modelled defects and connected them to the ones present in the experiments. By determining the scattering matrix elements of these defects, I calculated their specific Raman spectra. Finally, by comparing the spectra I gave guidelines to distinguish between the contributions of the different kind of defects [R3].

3 Publications

3.1 Publications used in the thesis points

[R1] G. Kukucska and J. Koltai:
"Theoretical investigation of strain and doping on the Raman spectra of monolayer MoS_2"

Physica Status Solidi B 254, No. 12, 1700184 (2017)
DOI 10.1002/pssb.201700184

[R2] G. Kukucska, V. Zólyomi and J. Koltai:
"Characterization of epitaxial silicene with Raman spectroscopy"

Phys. Rev. B 98, 075437 (2018)
DOI 10.1103/PhysRevB.98.075437

[R3] G. Kukucska, V. Zólyomi and J. Koltai:
"Resonant Raman spectroscopy of silicene and germanene"

ArXiv:1808.01354 [Cond-Mat], August (2018).

Under consideration at Journal of Physical Chemistry C

3.2 Additional publications

[S1] G. Kukucska, J. Koltai and J. Kürti:
"Stokes–anti-Stokes contribution to double resonance Raman processes in graphene"

Physica Status Solidi B 12, 2525-2529 (2014)
DOI 10.1002/pssb.201451227

[S2] P. Nemes-Incze, G. Kukucska, J. Koltai, J. Kürti, C. Hwang, L. Tapasztó and L. P. Biró:
"Preparing local strain patterns in graphene by atomic force microscope based indentation"

Scientific Reports 7, 3035 (2017)
DOI 10.1038/s41598-017-03332-5

[S3] P. Kun, G. Kukucska, J. Koltai, J. Kürti, L. P. Biró, L. Tapasztó, and P. Nemes-Incze:
"Strong Intravalley Scattering on Graphene Corrugations Revealed by Raman Spectroscopy."

ArXiv:1801.08861 [Cond-Mat], January (2018).

Under consideration at 2D Materials and Applications

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," *Science*, vol. 306, no. 5696, pp. 666–669, 2004.

[2] P. De Padova, C. Quaresima, C. Ottaviani, P. M. Sheverdyaeva, P. Moras, C. Carbone, D. Topwal, B. Olivieri, A. Kara, H. Oughaddou, B. Aufray, and G. Le Lay, "Evidence of graphene-like electronic signature in silicene nanoribbons," *Applied Physics Letters*, vol. 96, p. 261905, June 2010.

[3] N. D. Drummond, V. Zólyomi, and V. I. Fal'ko, "Electrically tunable band gap in silicene," *Physical Review B*, vol. 85, no. 7, p. 075423, 2012.

[4] M. Houssa, G. Pourtois, V. V. Afanas'ev, and A. Stesmans, "Electronic properties of two-dimensional hexagonal germanium," *Applied Physics Letters*, vol. 96, p. 082111, Feb. 2010.

[5] Y. Xu, B. Yan, H.-J. Zhang, J. Wang, G. Xu, P. Tang, W. Duan, and S.-C. Zhang, "Large-Gap Quantum Spin Hall Insulators in Tin Films," *Physical Review Letters*, vol. 111, p. 136804, Sept. 2013.

[6] Z. Zhu and D. Tománek, "Semiconducting Layered Blue Phosphorus: A Computational Study," *Physical Review Letters*, vol. 112, p. 176802, May 2014.

[7] R. M. A. Lieth and J. C. J. M. Terhell, "Transition Metal Dichalcogenides," in *Preparation and Crystal Growth of Materials with Layered Structures*, Physics and Chemistry of Materials with Layered Structures, pp. 141–223, Springer, Dordrecht, 1977.